EXHIBIT D

Introduction to the Principles of Ceramic Processing

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Dedicated to Carol and Scott

either the coalescence of pores on the boundary or the diffusion of vacancies from smaller pores to larger pores rather than to the grain boundaries, which is called Ostwald ripening.

In the final stage of sintering, exaggerated grains separated from pores commonly appear in some regions of the microstructure when the processing is not carefully controlled. The tendency for exaggerated grains is higher when powder aggregates or dense, extremely coarse particles are present and the pore distribution is inhomogeneous. A high sintered density with minimal grain growth occurs when the material contains fine particles packed very densely and when an additive called a grain growth inhibitor is dispersed and homogeneously distributed. A classic grain growth inhibitor is MgO in alumina, which apparently inhibits exaggerated grain growth by increasing D_s and consequently M_p;[*] when this system is sintered in an appropriate atmosphere, the density may exceed 99.9%. Small second-phase solid inclusions on the boundaries (Fig. 26.11) may also retard grain growth when the pores disappear, as has been demonstrated in yttria doped with La_2O_3 and ferrites and silicon nitride doped with Y_2O_3.[†] The general combinations of grain size and pore size for regular (pore-boundary attachment) and exaggerated (pore-boundary separation) grain growth and the effect of an inhibitor that reduces M_b are illustrated in Fig. 26.12.

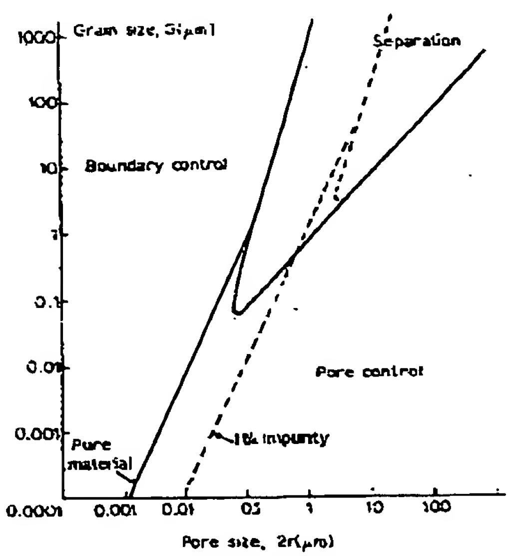

Fig. 26.12 Dependence of pore-boundary interaction on microstructural parameters in a system where the pores move by surface diffusion. (Reproduced with permission from R. J. Brook, *J. Am. Ceram. Soc.* 52(1), 57 (1969).)

[*] K. A. Berry and M. P. Harmer, *J. Am. Ceram. Soc.* 69(2), 143–149 (1986).
[†] M. F. Yan, Chapter 6 in *Advances on Power Technology*, G. Y. Chin (ed), American Society for Metals, Metals Park, OH, 1982.

A rapid heating schedule may produce densification with a smaller concomitant grain size. Surface diffusion, which predominates at low temperatures, can cause grain coarsening; when fast heating increases the vacancy diffusivity (D_v) and densification at a faster rate than diffusion causing grain coarsening, fast firing with a minimum isothermal hold at the maximum temperature should be beneficial.

The atmosphere is also important in sintering. Gas trapped in closed pores will limit pore shrinkage unless the gas is soluble in the grain boundary and can diffuse from the pore. Alumina doped with MgO can be sintered to essentially zero porosity in an atmosphere of H_2 or O_2, which are soluble, but not in air, which contains insoluble nitrogen. Insoluble gas evolved into pores, such as SO_2 or Cl_2 from anion impurities in powders, may also limit pore shrinkage. The density of oxides sintered in air is commonly less than 98% and often only 92–96%. The sintering atmosphere is also important in that it may influence the sublimation or the stoichiometry of the principal particles or dopant. The oxygen pressure and partial pressure of PbO and ZnO must be controlled when sintering compounds such as lead titanates and zinc ferrites, because incongruent vaporization may produce PbO or ZnO vapor. The sublimation rate is lower when the oxygen pressure is higher and in a closed sagger saturated with the vapor. However, chromic oxide (Cr_2O_3) can be densified only on sintering at a low oxygen pressure (10^{-10} to 10^{-11} atm), because in an oxidizing atmosphere it sublimates as CrO_2 or CrO_3.[*] In ceramic ferrites, the oxidation state of the transition metal ions and lattice vacancies depend on the sintering atmosphere, and the partial pressure of oxygen is controlled to obtain a high density and the proper magnetic phases. When sintering nonoxide ceramics

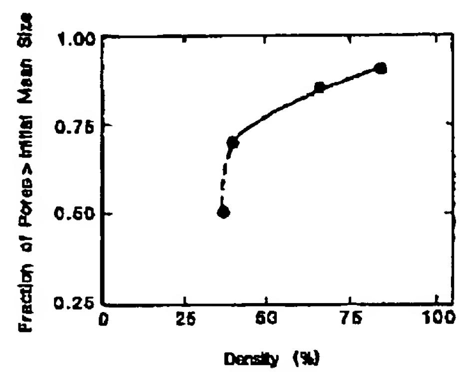

Fig. 26.13 On sintering an inhomogeneous compact of submicron zirconia powder, pores larger than the grain size shrink relatively slowly and persist, and the apparent mean pore size determined by mercury porosimetry increases on densification.

[*] H. U. Anderson, *J. Am. Ceram. Soc.* 57(9), 34–37 (1974).